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Determination of overpotential characteristics of reversible solid oxide cells via impedance spectroscopy and correlation with cell degradation

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Determination of overpotential characteristics of reversible solid oxide cells via impedance spectroscopy

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Risø DTU
National Laboratory for Sustainable Energy

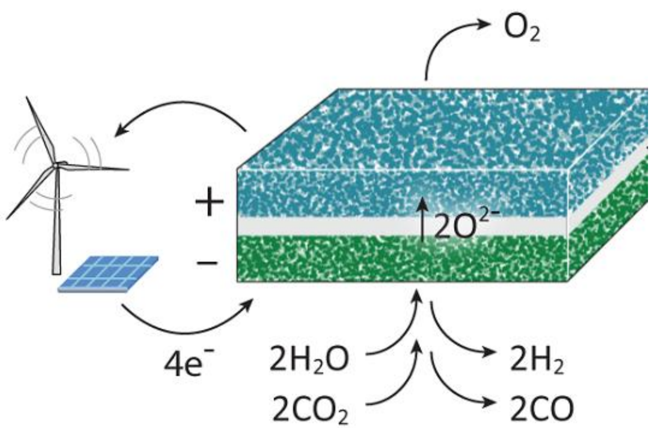
Outline

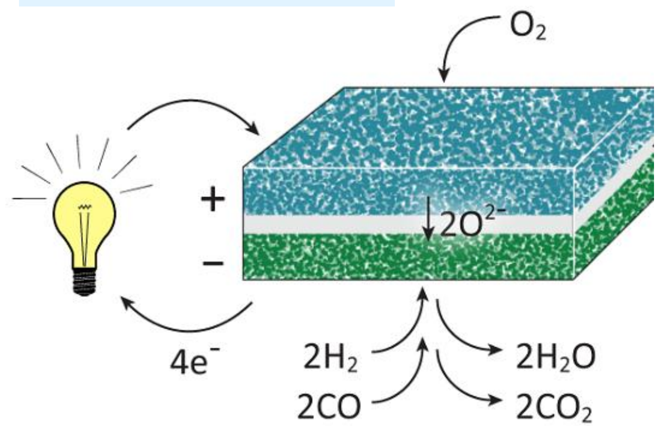
- Introduction + Purpose
- Experimental
- Results + Modeling
- Applications
- Conclusions

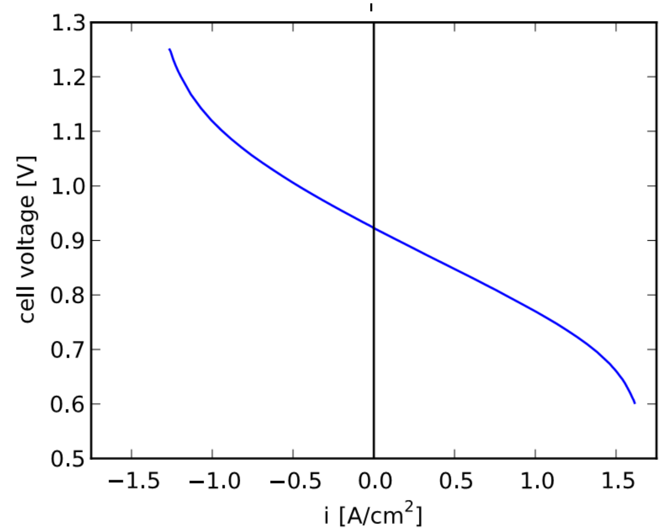
Introduction + Purpose

- Solid oxide cells promise economical + efficient sustainable energy conversion

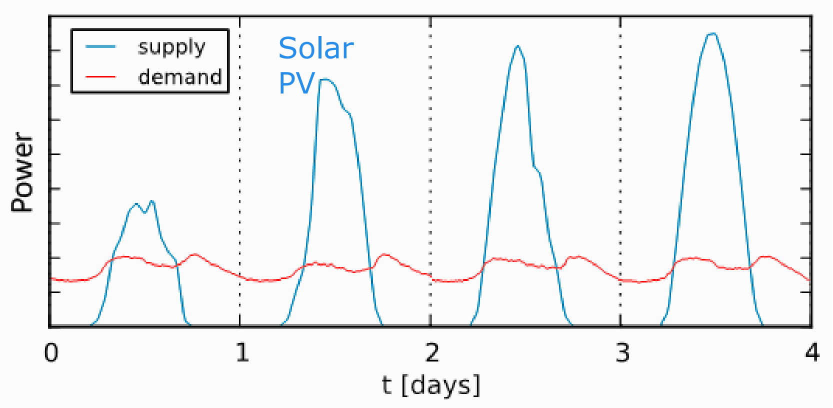
Electrolysis mode	Fuel cell mode
electricity → fuels	fuels → electricity







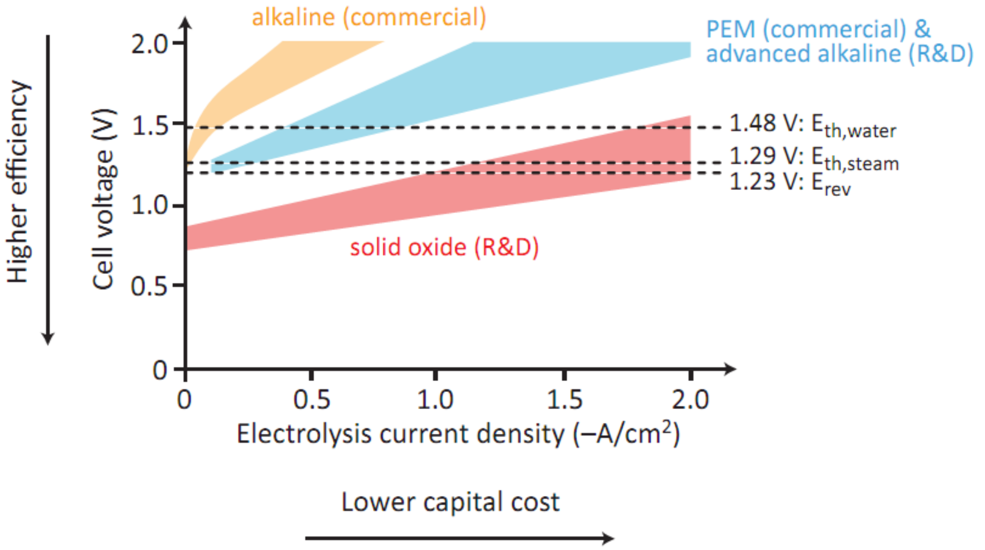
Introduction + Purpose



Economical energy storage is ultimately needed to scale up renewable energy to meet a significant fraction of demand

High temp. co-electrolysis of H_2O + CO_2

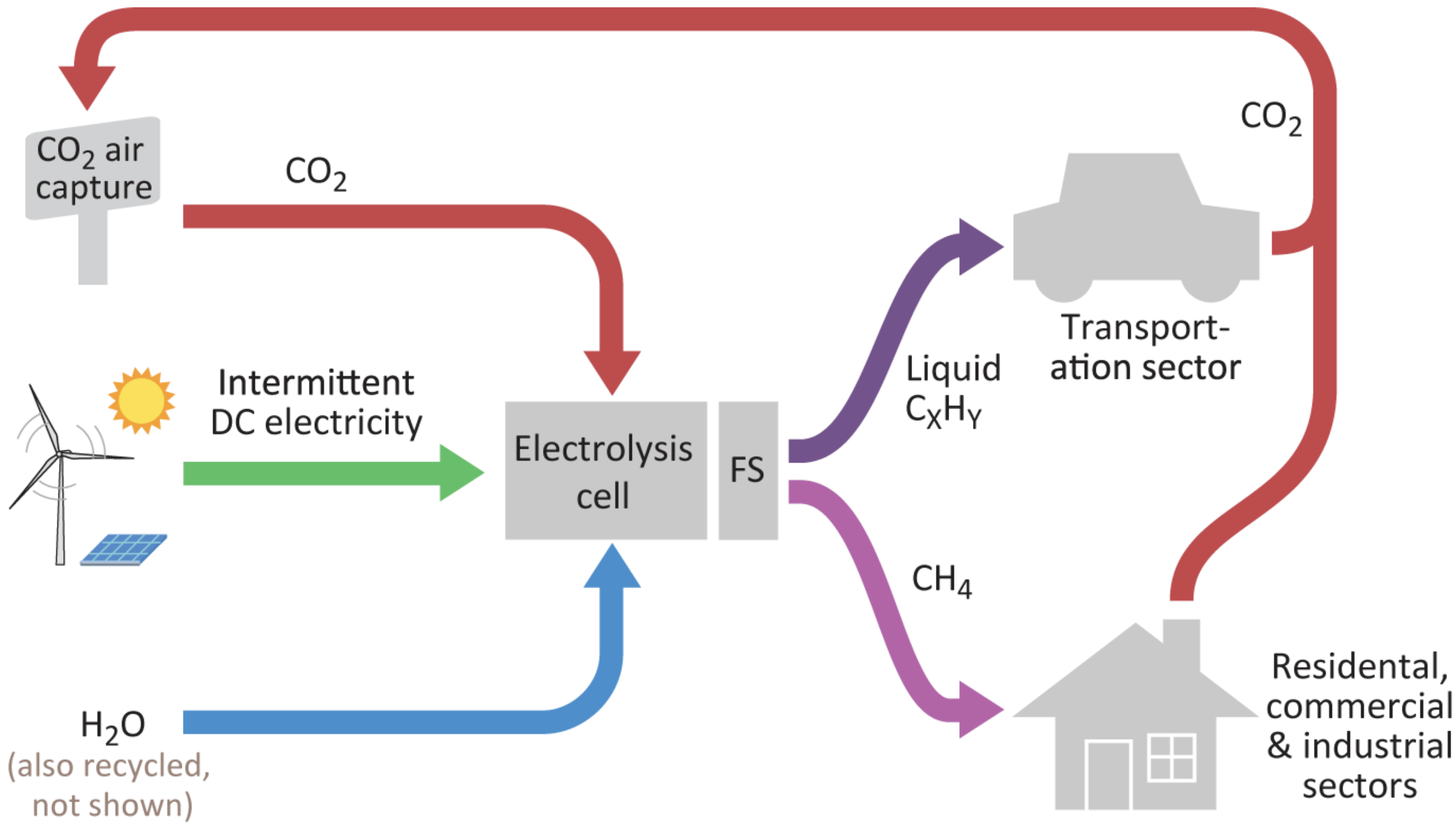
- makes very efficient use of electricity + heat (near-100% electricity-to-syngas efficiency)
- provides high reaction rates
- directly produces syngas (CO/H_2 mixture) for use in conventional catalytic fuel synthesis reactors.



[C. *Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, Renewable and Sustainable Energy Reviews 15 (2011) 1-23*]

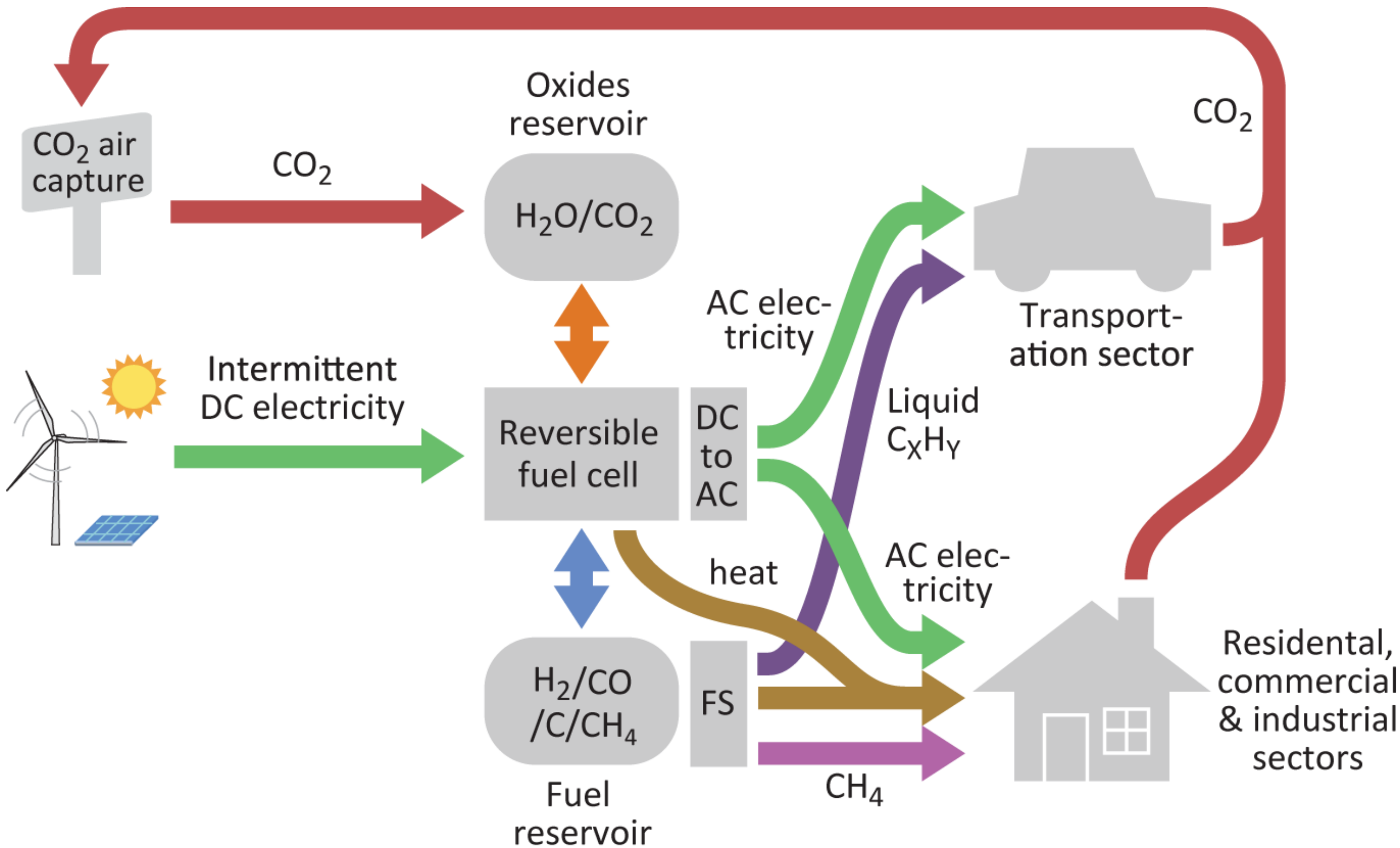
Electrolysis cells

Intermittent electricity → hydrocarbon fuels



Reversible fuel cells

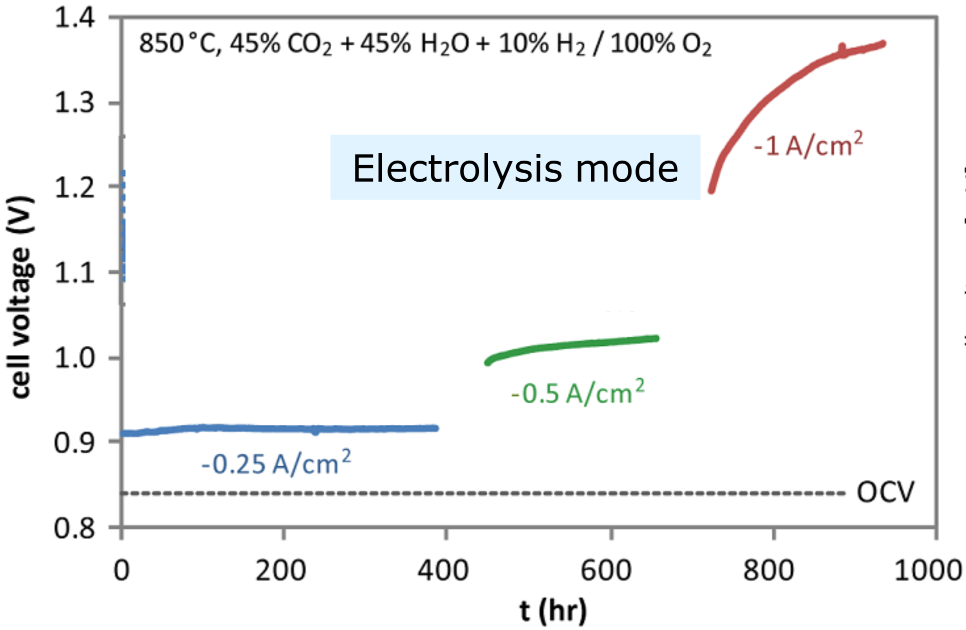
Intermittent electricity → hydrocarbon fuels + on-demand electricity



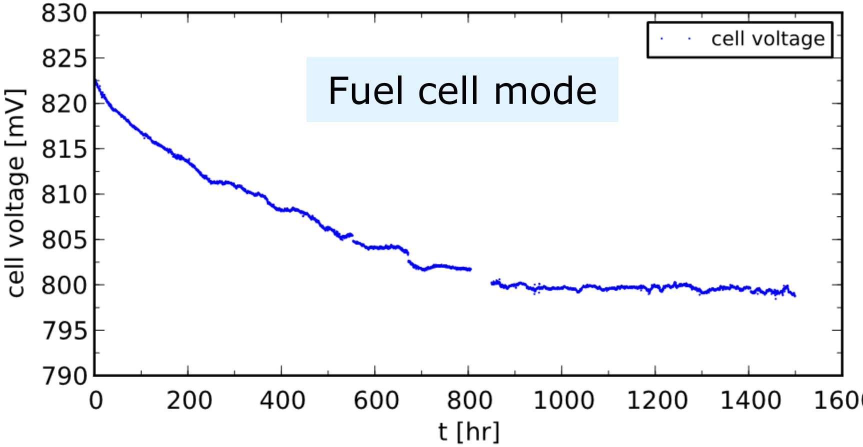
Introduction + Purpose

Solid oxide cells

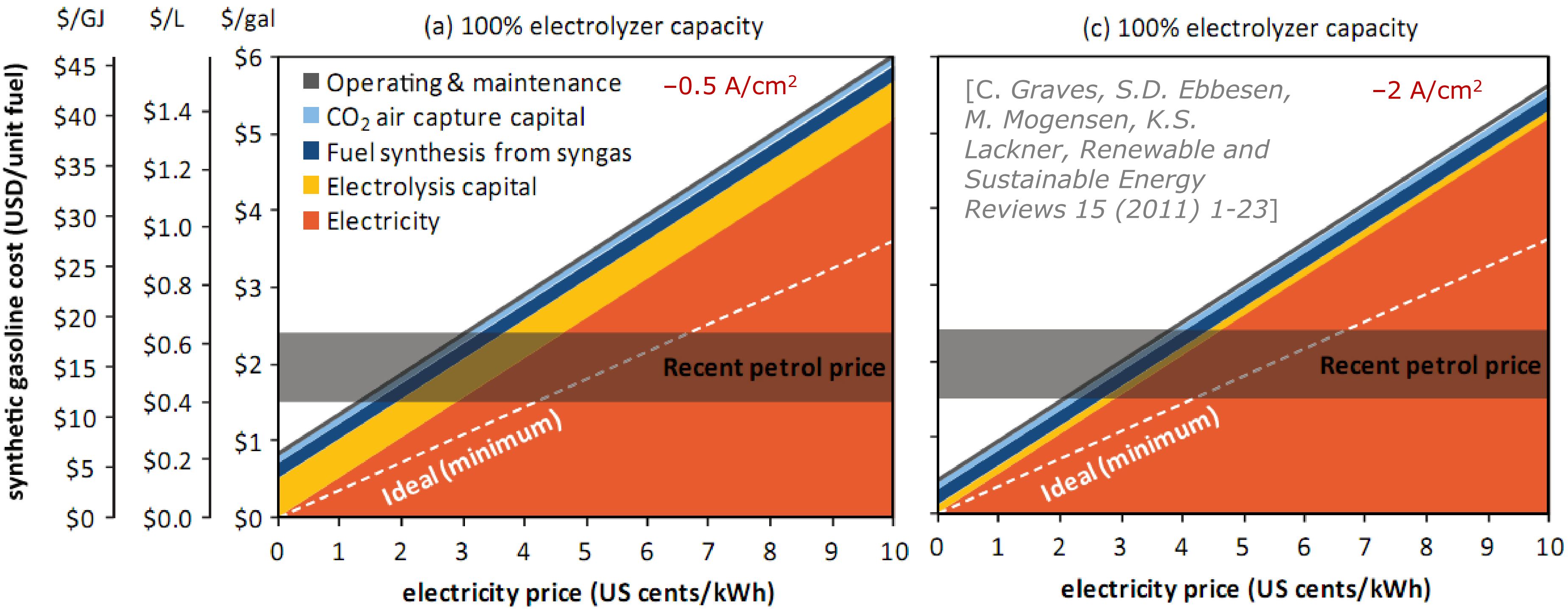
- High performance for reversible reactions
  - Oxidation of $H_2/CO/CH_4$
  - Reduction of H_2O/CO_2
- Important goal is improving long-term durability



From: **Graves C**, Ebbesen SD, and Mogensen M, "Co-electrolysis of CO_2 and H_2O in Solid Oxide Cells: Performance and Durability," *Solid State Ionics* 192(1): p. 398-403 (2011).



Importance of current density

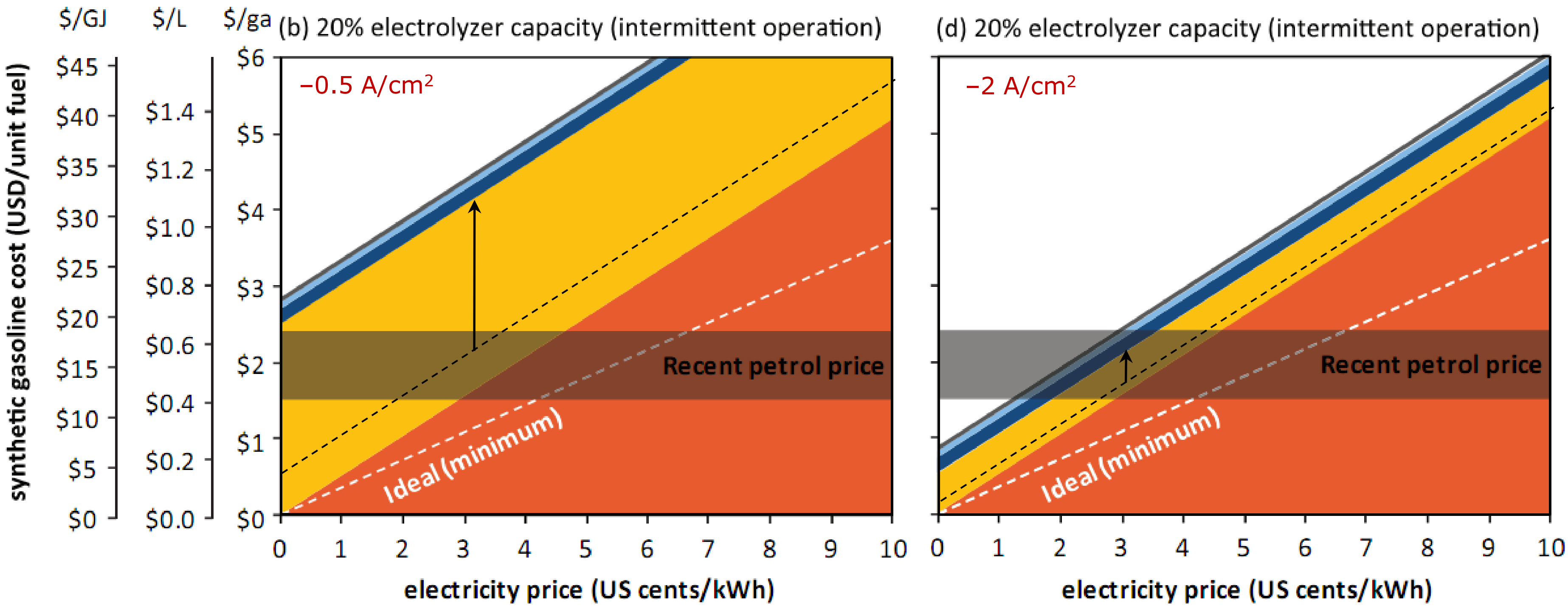


Fuel production economics is promising…

Re. choice of "safe" and "harsh" current densities:

- *Graves, Ebbesen, Mogensen 2010 doi: 10.1016/j.ssi.2010.06.014*
- *Xiufu Sun's talk tomorrow*
- *Knibbe, Traulsen, Hauch, Ebbesen, Mogensen 2010 doi: 10.1149/1.3447752*
- *Ebbesen, Graves, Hauch, Jensen, Mogensen 2010 doi: 10.1149/1.3464804*
- *Ebbesen & Mogensen 2010, doi: 10.1149/1.3455882*

Importance of current density & capacity factor



Introduction + Purpose

Degradation of cell components is related to voltage across each component

- Fuel cell mode: too high anodic overpotential for Ni → NiO
- Electrolysis mode: too high anodic overpotential for oxygen electrode → microstructural degradation at interface with electrolyte

Normally, measuring overpotentials requires a reference electrode

- Here we demonstrate calculation of component-wise overpotentials (e.g. across each electrode and the electrolyte) for fuel cell + electrolysis polarization
  - without using a reference electrode
  - by careful measurement + analysis of impedance data
  - Also facilitates study of electrode kinetics

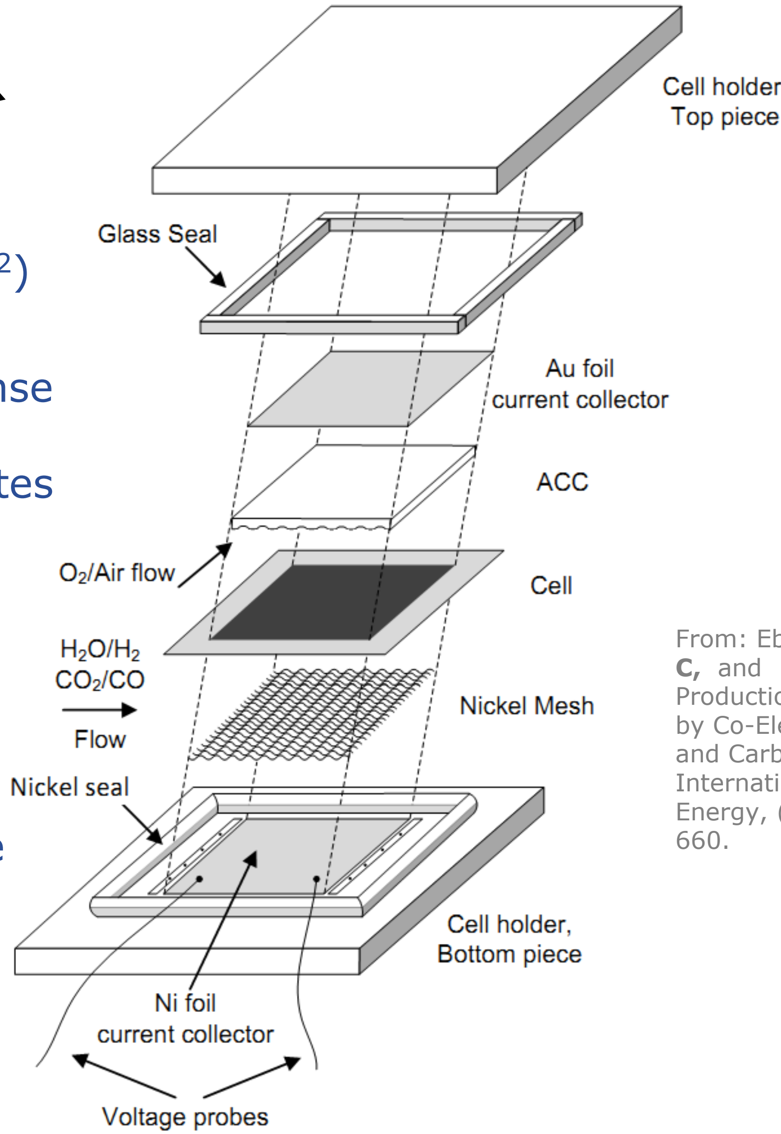
See also recent work by Leonide and coworkers:

Leonide A, Apel Y, and Ivers-Tiffee E, ECS Transactions, (2009). 19(20): 81-109.

A. Leonide et al., Journal of Power Sources, (2011). 196(17): 7343-7346.

Experimental

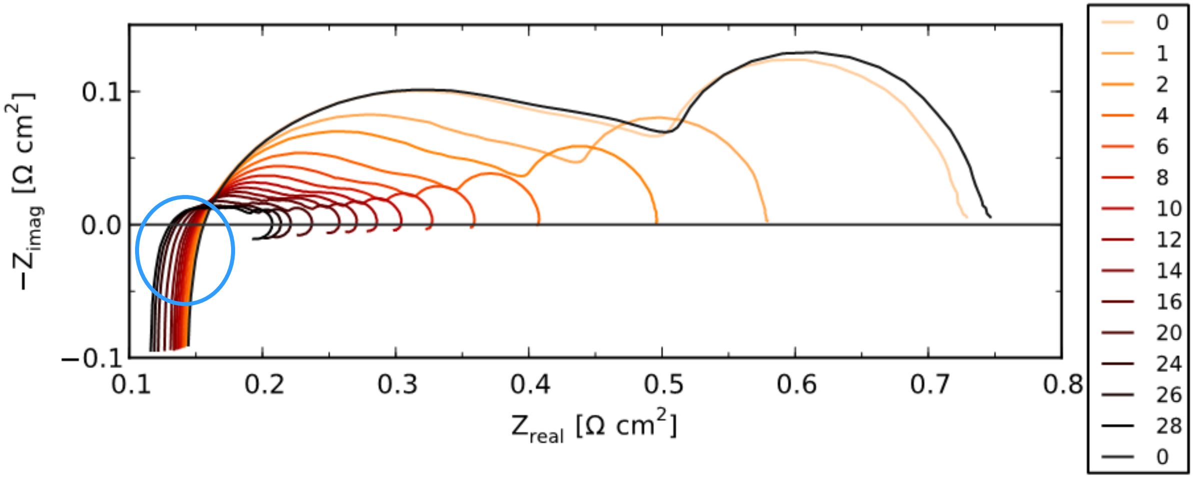
- Test set-up similar to
- Cell type:
  - Most measurements on Ni-YSZ/YSZ/CGO/LSC (16 cm^2)
  - LSC oxygen electrode chosen because its impedance response has less overlap with other impedance processes (facilitates fitting impedance data)
- Test conditions:
  (impedance data measured at)
  - 650 – 850 °C
  - Varying $H_2/CO/H_2O/CO_2$ compositions to fuel electrode and pO_2 to ox. electrode
  - Varying current density



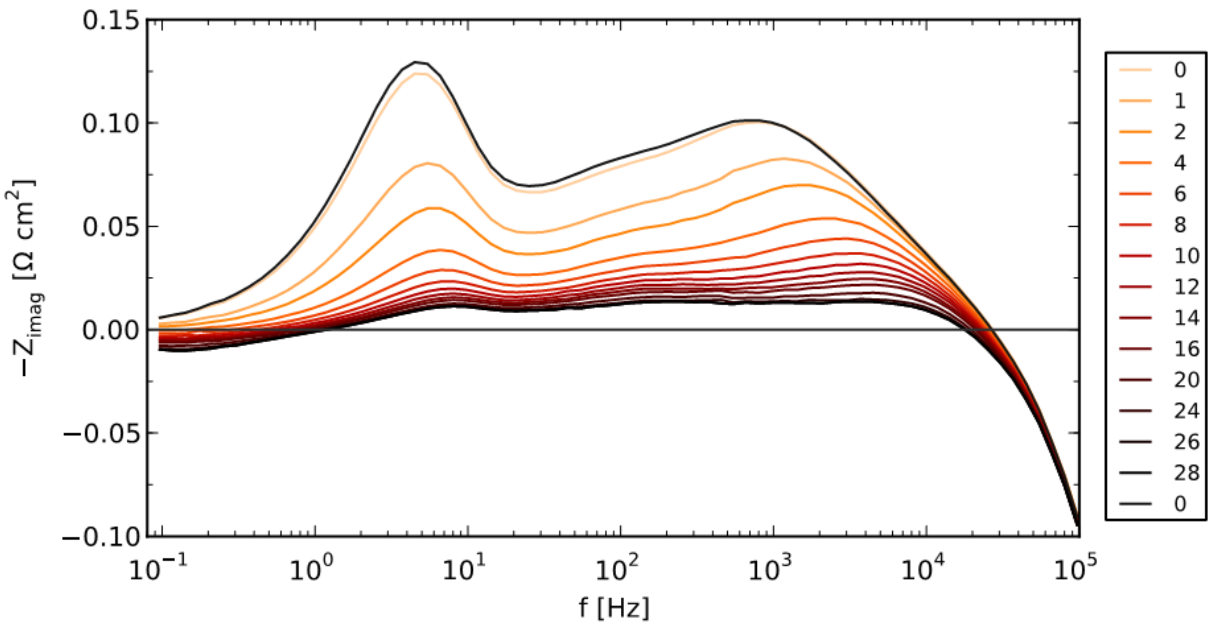
From: Ebbesen SD, **Graves C,** and Mogensen M, Production of Synthetic Fuels by Co-Electrolysis of Steam and Carbon Dioxide. International Journal of Green Energy, (2009). 6(6): p. 646 – 660.

Results

- Fuel cell mode – impedance measured under polarization

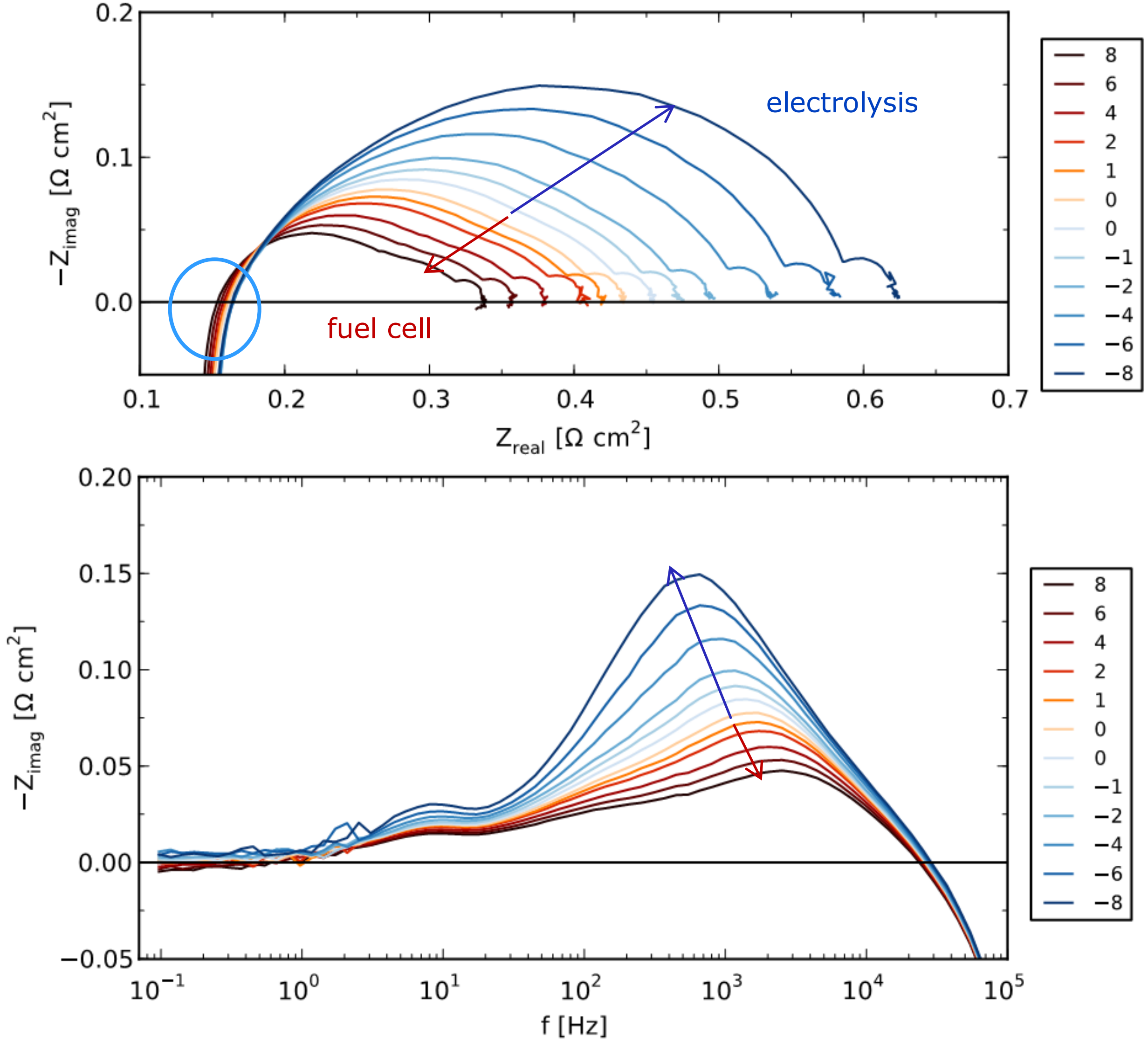


750 °C,
H_2/H_2O=97/3,
ox.el.=air



Results

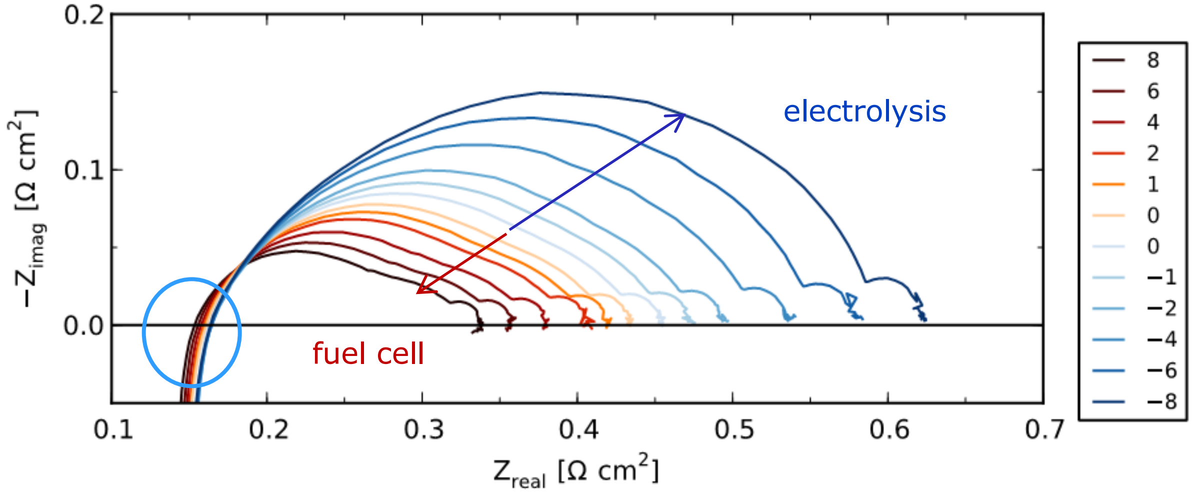
- Reversible – impedance measured under polarization



750 °C,
H_2/H_2O=50/50,
ox.el.=air

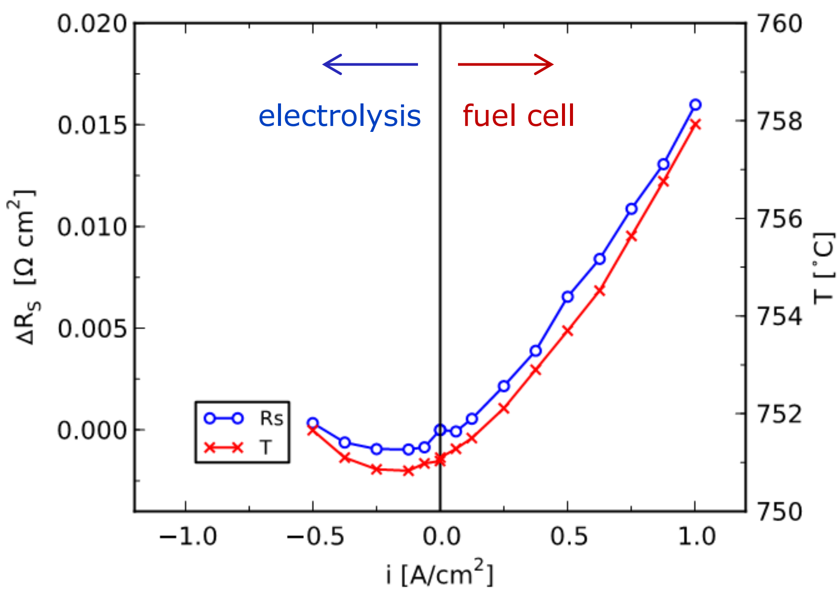
Results

- Impedance measured under polarization



750 °C,
H_2/H_2O=50/50,
ox.el=air

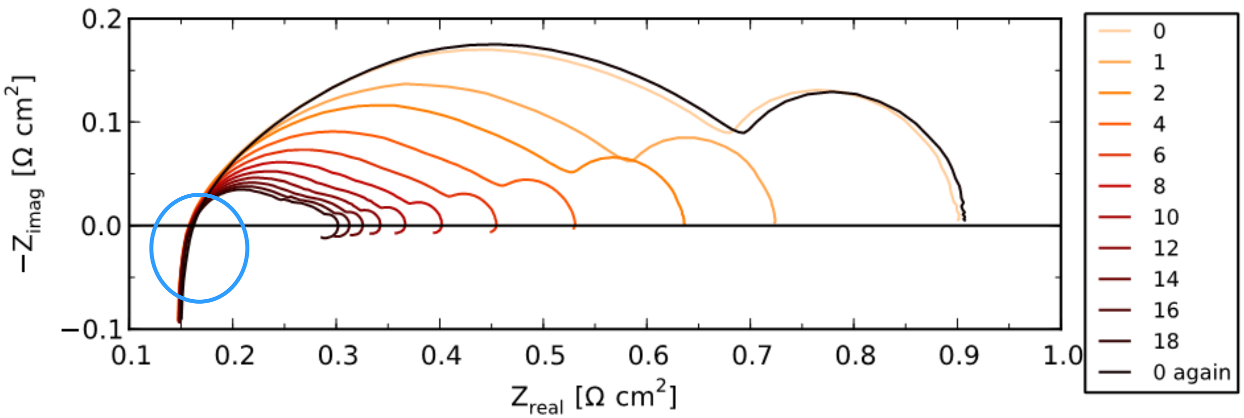
R_S is affected by temperature changes e.g. heating especially during fuel cell polarization



Using electrolyte conductivity activation energy of 0.8-0.9 eV for R_S, ΔT accounts for ΔR_S, approximately (calculated ΔT is slightly higher than measured ΔT; thermo-couple is ~1mm from electrolyte which can account for this)

Results

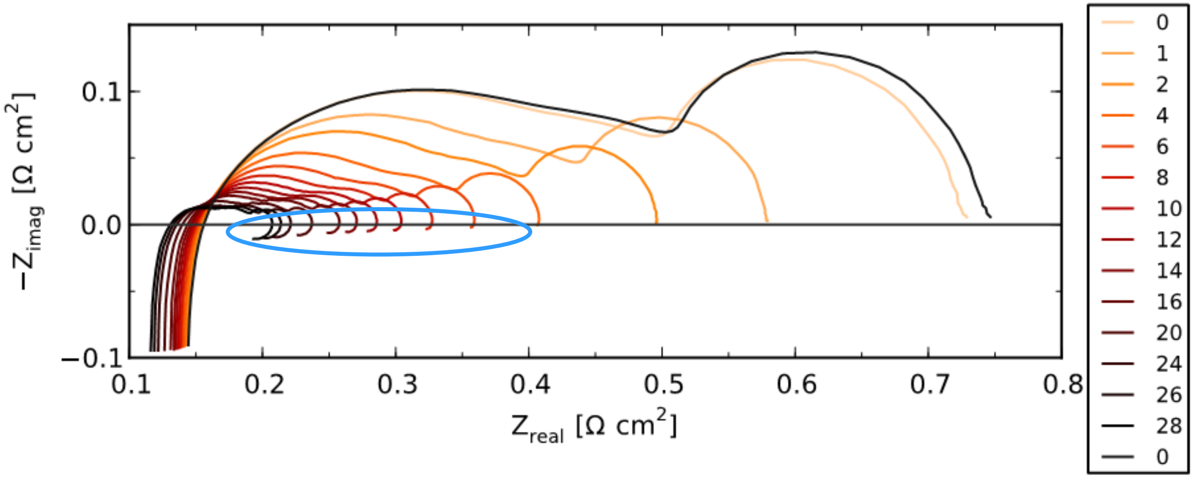
- Those were ”fixed oven temperature” measurements
- The heating/cooling upon polarization effects temperature activated processes e.g. electrode kinetics
- This effect can be compensated for by using R_S as a temperature indicator and adjusting the oven temperature at each load setting, to obtain ”fixed cell temperature” (fixed R_S) measurements:



750 °C,
H_2/H_2O=97/3,
ox.el=air

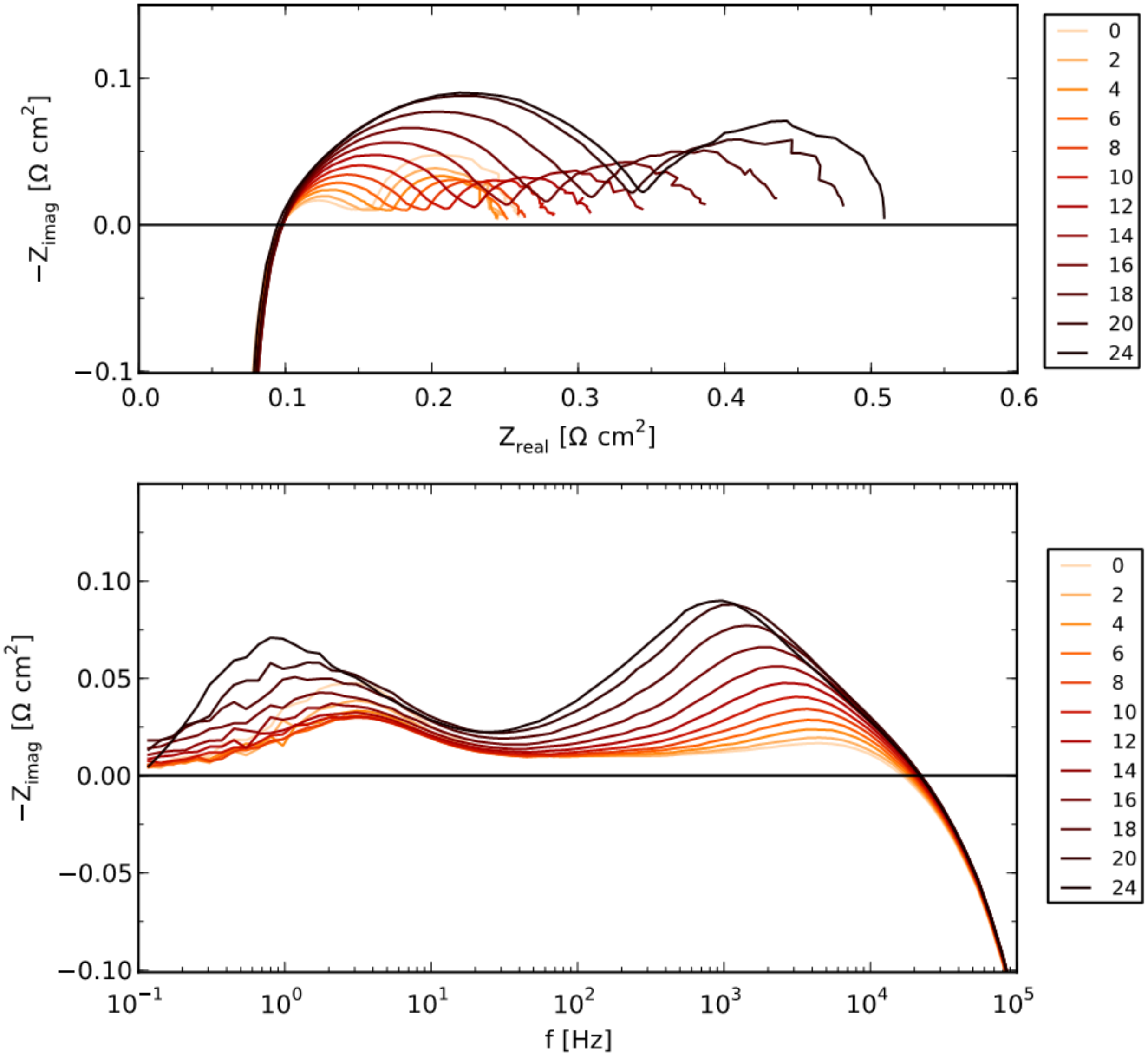
Modeling the impedance data

- To quantify resistance contributions from each cell component, the impedance data must be carefully modeled
- Equivalent circuits or models based on chemical/physical processes
- Today all results used an equivalent circuit based on a previous equivalent circuit model established for Ni-YSZ/YSZ/LSM-YSZ type cells, now with a Gerischer element for oxygen electrode;
  we are also fitting to a model without circuit elements
- The low-frequency inductive loop observed at high current densities/overpotentials in both fuel cell & electrolysis modes has been speculated as various adsorption/surface layer processes. It affects quantifying the gas concentration process and should be included in the model



Modeling the impedance data

- Co-electrolysis – impedance measured under polarization

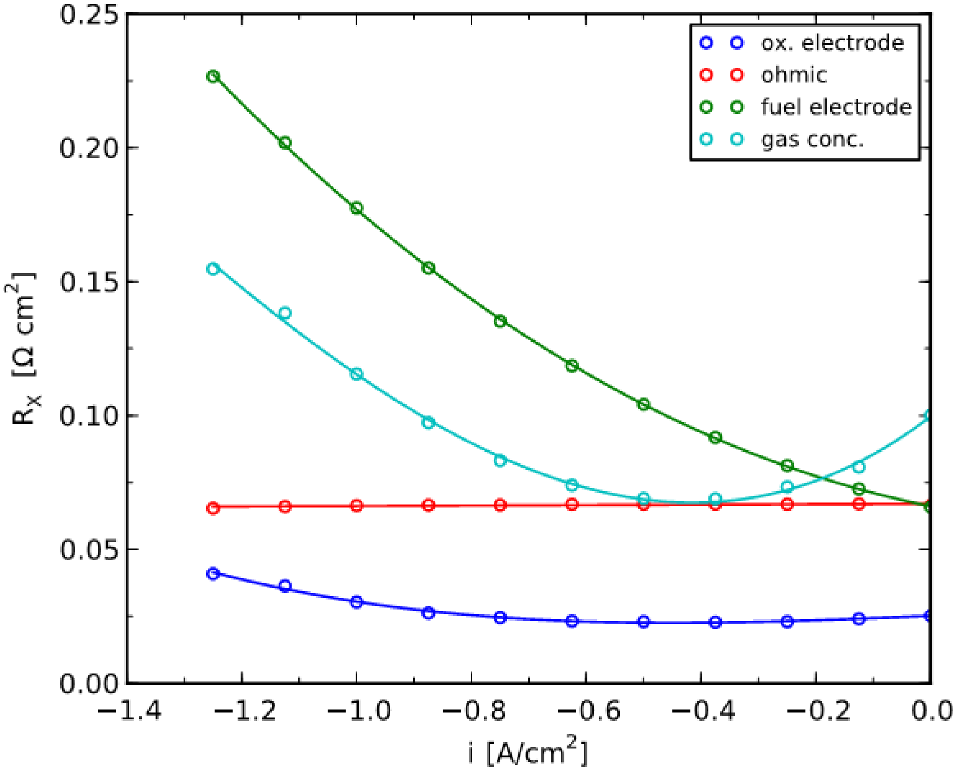


800 °C,
co-electrolysis
90%-reactants
(CO_2+H_2O),
ox.el.=O_2

Modeling the impedance data

- Co-electrolysis – impedance measured under polarization

Break down of cell resistance



800 °C,
co-electrolysis
90%-reactants
(CO_2+H_2O),
ox.el.=O_2

Calculating overpotential curves from fitted data

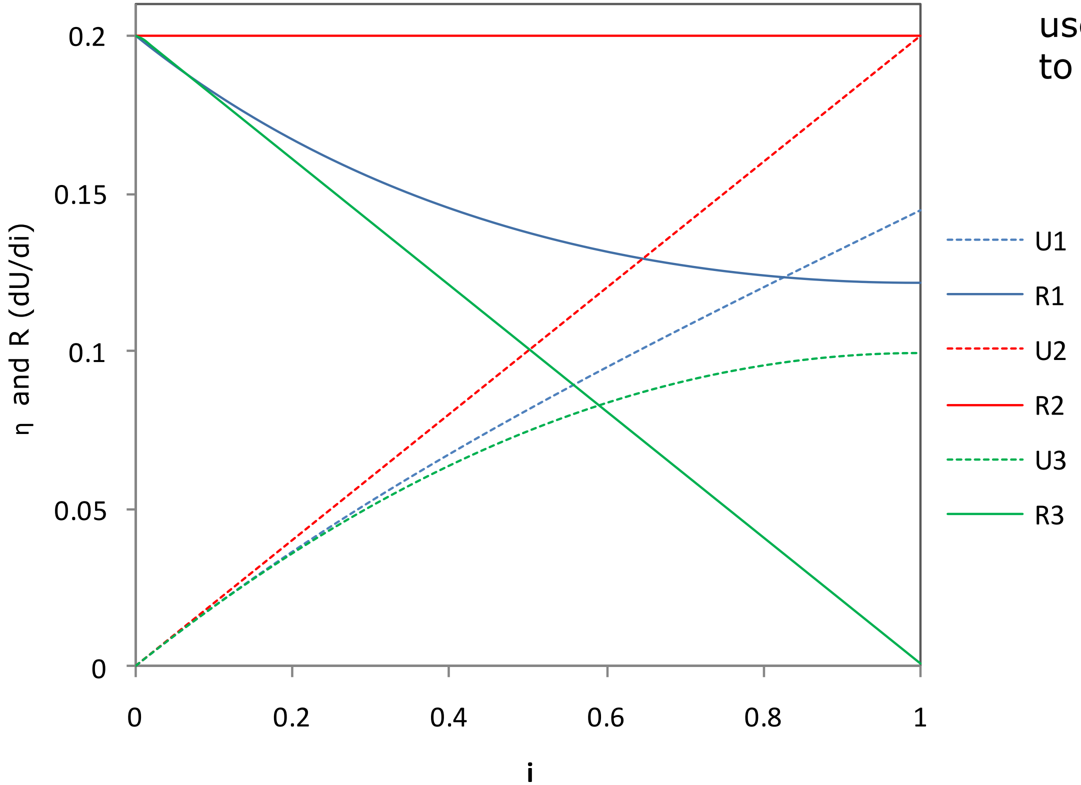
Meaning of $R_{X,EIS}$ vs i

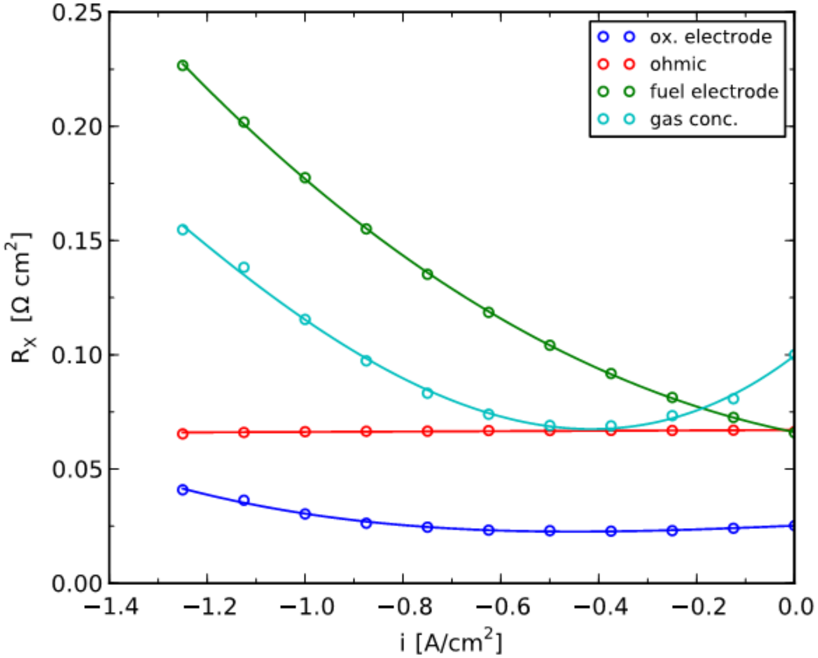
$R_{EIS} = dU/di$ (local slope of an i-U curve)

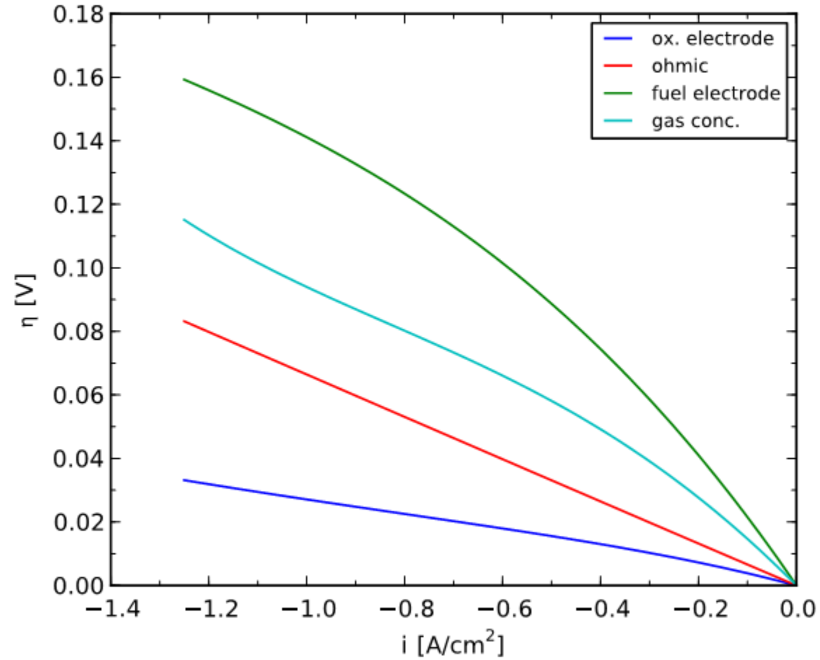
To recreate an i-U curve, $dU = R_{EIS} \cdot di$, so integrate,
or numerically each $U_n = U_{n-1} + R_{EIS,n} \cdot (i_n - i_{n-1})$

Since we have a limited number of data points, use a fit (spline) to i-R curves

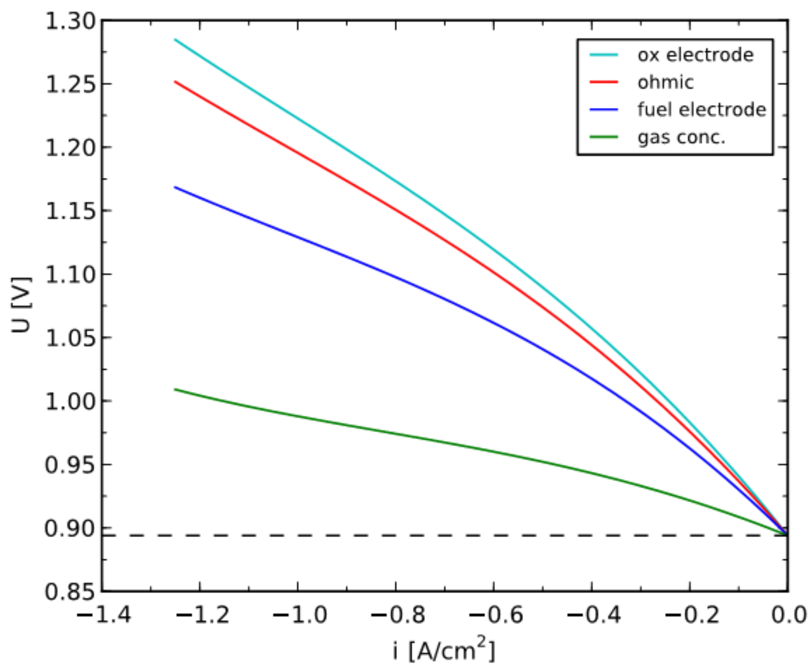
What does it look like? Examples







Break down of overpotentials

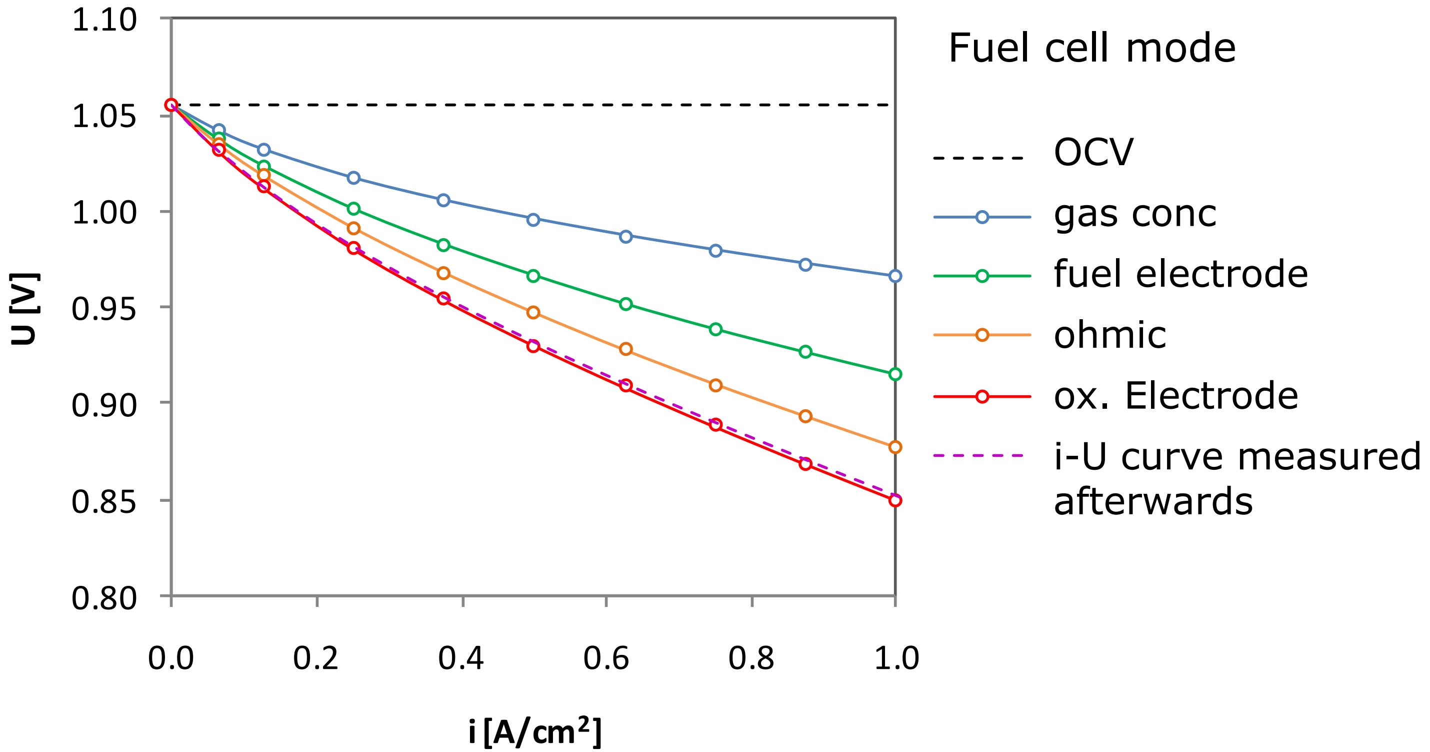


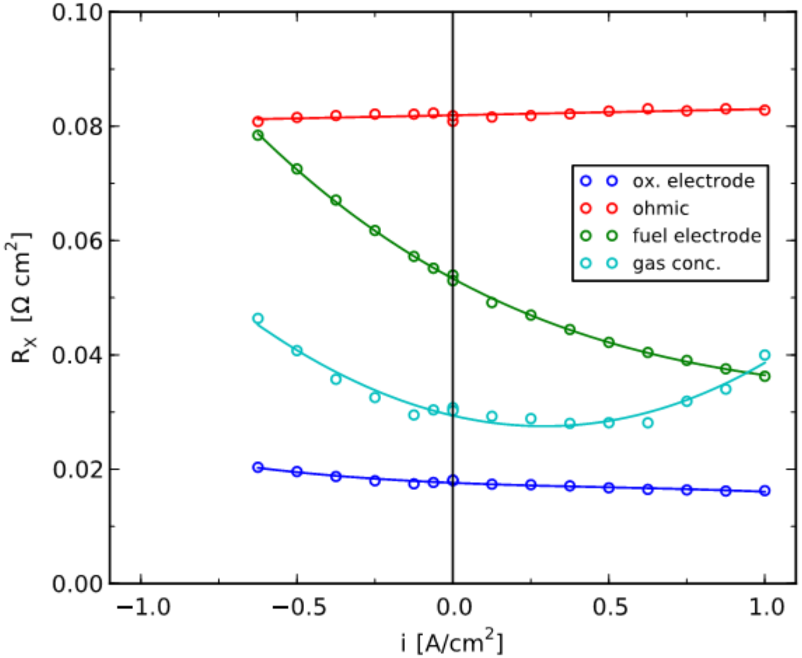
800 °C,
co-electrolysis
90%-reactants
(CO_2+H_2O),
ox.el.=O_2

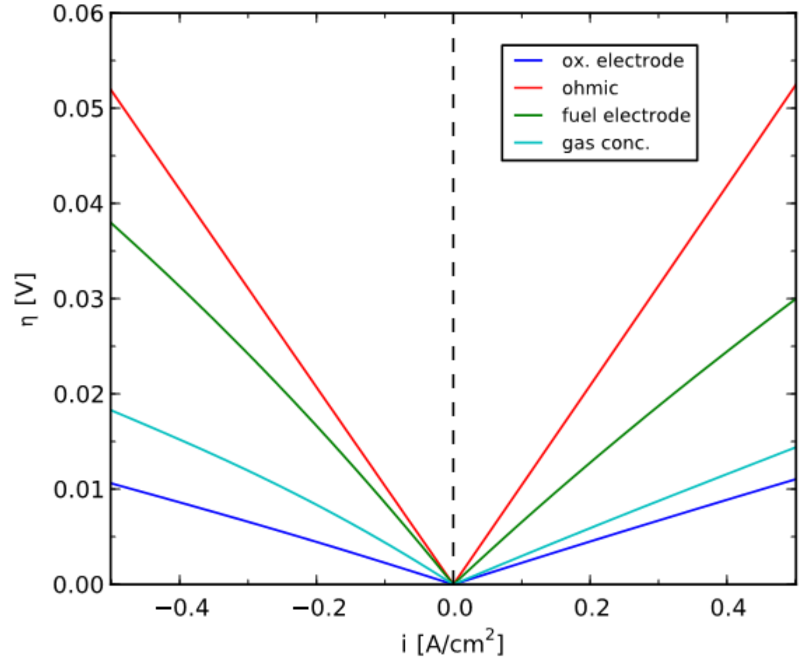
Added to OCV to obtain calculated i-U curve

Calculating overpotential curves from fitted data

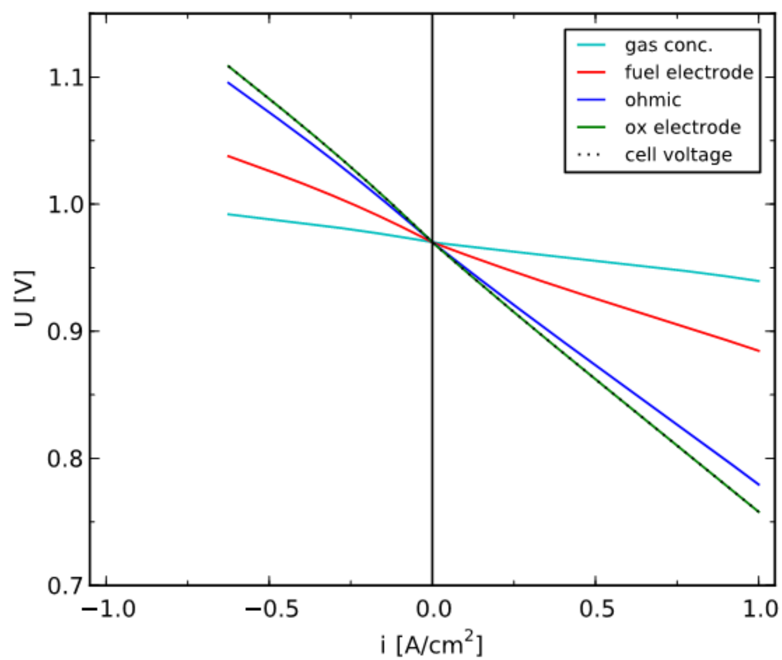
Overlaid on measured i-U curve → agreement
(it had better agree if the method works ☺)







Reversible
polarization
- asymmetry



800 °C,
H_2/H_2O=50/50,
ox.el.=O_2

Further considerations

- Effect of number data points (errors that arise)
- Effect of level of detail of model (errors)

Applications

- Overpotential vs time (degradation)
- Obtaining electrode kinetics parameters
- Connecting/reconciling DC and AC measurements (shown in earlier slide)
- Determine safe operating conditions (avoiding Ni/NiO)
- Comparing with 3-electrode measurements to study ref. electrode effects

Conclusions

- Analysis method demonstrated for electrolysis + fuel cell operation
  - careful measurement + analysis of impedance data obtained on full cells → calculate overpotential-current curves
- Isothermal i-U measurements obtained
  - and procedure developed
  - enables more meaningful study of transport/kinetics parameters
- Method being applied to long-term durability tests to calculate overpotential across each component during testing (observe evolution of overpotentials) and correlate with cell degradation

Acknowledgements

- Xiufu Sun for some of the measurements
- Energinet.dk
- SERC.dk
- Topsoe Fuel Cell

Thank you!